A Kinetic Study of the Decomposition of HNO_3 and its Reaction With NO

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Abstract

The rate of reaction between NO and HNO_3 and the rate of thermal decomposition of HNO_3 have been measured by FTIR spectroscopy. The measurements were made in a teflon lined batch reactor having a surface to volume ratio of 14 m^{-1}. During the experiments, with initial HNO_3 concentrations between 2 and 12 ppm and NO concentrations between 2 and 30 ppm, a reactant stoichiometry of unity and a first order NO and HNO_3 dependence were confirmed. The observed rate constant for the reaction

$$HNO_3 + NO \longrightarrow HNO_2 + NO_2$$

at 22°C and atmospheric pressure was determined to 1.1 (±0.3) 10^{-5} ppm^{-1} min^{-1}. At atmospheric pressure, HNO_3 decomposes into NO_2 and other products with a first order HNO_3 dependence and with a rate constant of 2.0 (±0.2) 10^{-3} min^{-1}. The apparent activation energy for the decomposition is 13 (±4) kJ mol^{-1}.

Introduction

HNO_3 is a strong acid which, when formed in the atmosphere, contributes to corrosion in urban areas and to acidification and damage to vegetation in the rural environment. The fate of gaseous HNO_3, originating from photochemical or thermal transformation of nitrogen oxides is therefore of considerable interest.

Few studies of the reduction of HNO_3 by NO have been made and the more recent rate and mechanism information is not consistent [1–3]. Furthermore, the reactant concentrations used in the present work were significantly lower and thus, closer to ambient concentrations than in any of the previous studies.

Another channel for loss of gaseous HNO_3 is through thermal decomposition into NO_2 and other products. In theory, given the proper conditions, such a reaction could serve as a source of NO_2 from a reservoir of HNO_3.

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Experimental

The experiments were made at atmospheric pressure in a batch reactor with N_2 as matrix gas. The cylindrical reactor was lined with .025 mm FEP teflon film except for the mirrors and the ir windows. The vessel has a volume of 0.153 m^3 and a S/V (surface to volume) ratio of 14 m^{-1}. The reactor can be evacuated with a two stage rotary vane pump to less than 5 Pa and is enclosed in an insulated box where the temperature may be controlled between 0 and 60 ± 1°C.

The HNO_3 used was prepared by vacuum distillation of mixtures of reagent grade $NaNO_3$ and H_2SO_4 and had a purity of 100.0 $\pm 0.5\%$. The NO used was >99.8% pure with NO_2 as the major impurity.

The introduction of known quantities of NO into the reactor was accomplished by filling the calibrated bulbs of a vacuum line gas handling system with NO to some predetermined pressure and then expanding the gas into the evacuated reactor. The pressure was measured with a Validyne CD 233 pressure gauge (0-18 kPa or 0-180 kPa). The HNO_3 vapor concentration was controlled by evaporation of carefully measured quantities of HNO_3.

The concentrations of HNO_3, HONO, NO_2, and NO were followed by FTIR spectroscopy. The reactor has, attached to the endplates, a three mirror White optical system [4] with a base path length of 2 m. The three glass mirrors, one of 0.21 m and two of 0.14 m diameter, are gold coated and have a protective layer of MgF_2. The mirrors may be adjusted by external controls to vary the number of reflexions. Path lengths between 8 and 120 m may be used. Infrared spectra of the reactor content were recorded with a Nicolet MX-1 Fourier Transform IR spectrometer coupled with a mirror arrangement to the reactor. A path length of 40 m was used in the experiments. The spectra were taken with 1 cm^{-1} resolution and collected from 4000 to 400 cm^{-1}. The time to collect a spectrum was 5 m. The box car apodization was used when calculating the spectra from the interferograms. The following frequencies and extinction coefficients were used to evaluate the concentrations:

NO_2 1599 cm^{-1} $\quad \sigma = 2.2(\pm 0.06)10^{-3}$ ppm^{-1} m^{-1}
(in house calibration)

trans-HONO 1264 cm^{-1} $\quad \sigma = 3.84(\pm 0.38)10^{-3}$ ppm^{-1} m^{-1}
with *trans*-HONO/*cis*-HONO = 2.29 to calculate total HONO [5].

NO 1876 cm^{-1} $\quad \sigma = 2.77(\pm 0.03)10^{-4}$ ppm^{-1} m^{-1} [6].

HNO_3 878 cm^{-1} $\quad \sigma = 1.75(\pm 0.18)10^{-3}$ ppm^{-1} m^{-1} [6].

$$(\ln(I_0/I) = \sigma c l)$$

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The smallest measureable concentrations in practical work with 40 m path length in this reactor are: NO 200 ppb, NO_2 60 ppb, HNO_3 40 ppb and *trans*-HONO 40 ppb.

The majority of the experiments were conducted as follows: Before the experiment the reactor was three times evacuated to 1 kPa and refilled with pure N_2, then again evacuated and a background spectrum collected.

If NO was used in the experiment, a measured amount was introduced from the gas handling system with N_2 as carrier until the reactor pressure was about 30 kPa. The HNO_3 vapor was then added to the reactor with a stream of N_2 until the reactor pressure was 100 kPa. The procedure took about 10 min from the first addition until the first spectrum had been collected. The collection of a spectrum was then initiated every 15 min for a total time of 180 min.

Changes in HNO_3, HONO, NO_2, and NO concentrations were evaluated by subtracting the zero time spectrum from subsequent spectra. The resulting difference spectra thus show a positive absorption band for an increasing concentration and vice versa (Fig. 1).

To obtain the quantity of interest, $d(NO_2)/dt*1/[HNO_3]$, the NO_2 formation rate was found as the tangent at time t to the NO_2 formation curve and was divided by the corresponding measured gas-phase HNO_3 concentration. Normally 11 such values of $d(NO_2)/dt*1/[HNO_3]$ were obtained per experiment.

To compare the measured HNO_3, HONO, NO_2, and NO data to proposed models, the resulting differential equations were integrated with FACSIMILE [7], a computer program for the solution of initial value problems arising as systems of differential equations. The program was also used to fit rate constants, by a least squares procedure, to the experimental data. Normally this was done to check the manual evaluation of the rate constants. The agreement between refined and manually obtained values was good.

Results and Discussion

HNO_3 Decomposition

Thermodynamic calculations show that the equilibrium mixture, resulting from HNO_3 in N_2 contains significant amounts of NO_2 and thus decomposition of HNO_3 is expected. Table I gives the calculated equilibrium composition of gas mixtures with various initial concentrations of the reactants. The calculations were based on enthalpy, entropy, and heat capacity data from Barin and Knacke [8] except for HONO where information from the JANAF tables, [9] was used. It may be noted that, also in an oxidizing atmosphere, a significant

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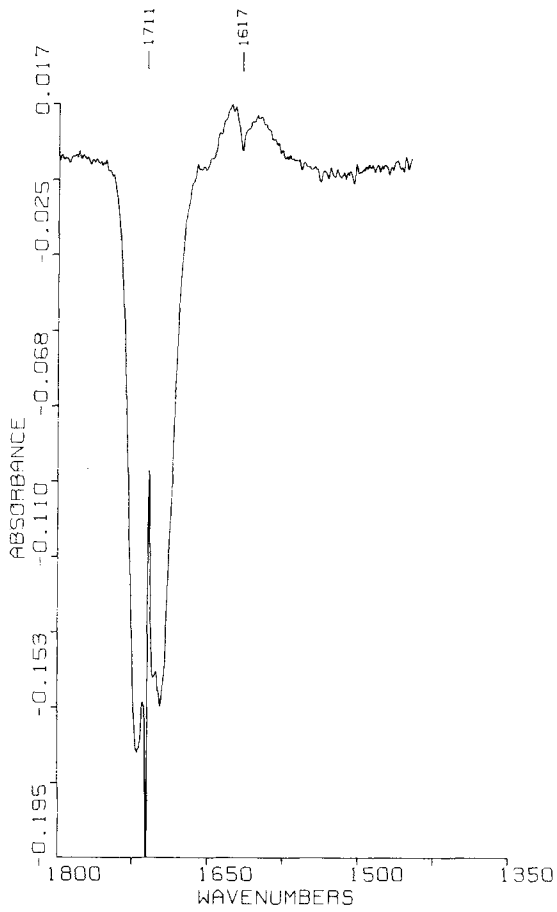

Figure 1. Difference spectrum, found by subtracting the initial reactant spectrum from the product spectrum. NO_2 1617 cm^{-1}; HNO_3 1711 cm^{-1}.

fraction of NO_2 is present together with the HNO_3 at equilibrium and that H_2O, O_2, and low temperature tends to stabilize HNO_3.

An initial set of experiments was made to quantify the chemical and physical behavior of HNO_3 in N_2 in the reactor. In agreement with earlier work [10–11], it was observed that HNO_3 was lost from the gas phase and that NO_2 was produced. The NO_2 produced was less than expected, had the HNO_3 lost decomposed quantitatively into NO_2.

The FEP-teflon lined walls of the reactor are known to adsorb HNO_3 from the gas phase [11] and the additional loss of HNO_3 is attributed to this phenomenon.

In two cases the reactor was opened after an experiment and a piece of the initially new and clean teflon film lining was rinsed with a small volume of water. The liquid was analyzed for inorganic anions

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TABLE I. Equilibrium partial pressures of some nitrogen compounds in gas mixtures with the given initial pressures of HNO_3, O_2, and H_2O in N_2 to give a total pressure of 1 bar. A number of other nitrogen species are present in very small concentrations at equilibrium. The notation $a(b)$ represents $a \times 10^b$ (1 bar = 10^5 Pa).

	Input Pressures (bar)			Equilibrium Pressures (bar)			
T(°C)	HNO_3	O_2	H_2O	NO	NO_2	HNO_2	HNO_3
2	8(-6)	0	3(-5)	5(-10)	7.2(-6)	3(-10)	79(-8)
20	8(-6)	0	3(-5)	2(-9)	7.8(-6)	4(-10)	20(-8)
38	8(-6)	0	3(-5)	9(-9)	7.9(-6)	5(-10)	7(-8)
20	8(-9)	0	3(-5)	7(-11)	7.9(-9)	2(-12)	3.4(-11)
20	8(-6)	0	1.6(-2)	2(-9)	5.3(-6)	6(-9)	2.6(-6)
20	8(-6)	2.1(-1)	3(-5)	5(-12)	5.5(-6)	1(-11)	2.5(-6)
20	8(-6)	2.1(-1)	1.6(-2)	7(-13)	0.7(-6)	4(-11)	7.3(-6)
20	8(-6)	5(-5)	3(-5)	5(-10)	7.6(-6)	2(-10)	0.4(-6)

by ion chromatography and the only species found was nitrate. In both cases the amount of nitrate on the reactor walls, extrapolated from the analysis, corresponded to about 65% of the starting material. Including the gas-phase nitrogen compounds at the end of the experiment, the material balance accounted for 93 and 104% of the starting material, respectively.

The yield of NO_2 (i.e. NO_2 formed/HNO_3 lost) varies with adsorption and reaction rate and thus with time during an experiment. Typically, the yield was 0.1 during the first 15 min and 0.8 during the last 15 min of an experiment.

Modelling exercises show that the adsorption may be reasonably well described by an adsorption step, first order in HNO_3 and a desorption step with a first order dependence on the surface concentration of HNO_3. The desorption rate depends on the initial surface concentration of HNO_3. Since the reactor clean-up procedure had problems with reproducing the remaining surface HNO_3 after cleaning, the analytical description of the HNO_3-time dependence becomes difficult. The change in HNO_3 concentration was therefore considered as unsuitable as a source of rate information.

The detailed mechanism for the HNO_3 decomposition at ambient temperature is not known, but the overall reaction is normally given as

$$(1) \qquad HNO_3 \longrightarrow NO_2 + \tfrac{1}{2}H_2O + \tfrac{1}{4}O_2$$

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The NO_2 production in our reactor follows first order kinetics with respect to HNO_3 for several hours as exemplified in Figure 2. In the following treatment, based on the above information, it is assumed that the thermal decomposition of one molecule of HNO_3 results in one molecule of NO_2, at a rate described by Eq. (I).

$$\text{(I)} \qquad d[NO_2]/dt = k_1[HNO_3]$$

Table II gives initial conditions and rate constants obtained from the HNO_3-only experiments. From experiments at different temperatures an apparent activation energy of 13 (±4) kJ mol^{-1} was calculated for reaction (1).

In references [1] and [3] HNO_3 is described as being stable over long periods of time at low total pressure. Our work shows that HNO_3 decomposes at atmospheric pressure. The decomposition rate may thus be pressure dependent. The remarkably low apparent activation energy of the decomposition process indicates that it is made up of several steps. One possible sequence is an adsorption/desorption step where the surface concentration decreases with temperature followed by a heterogeneous decomposition step, the rate of which increases with temperature. Since the two processes influence the observed rate

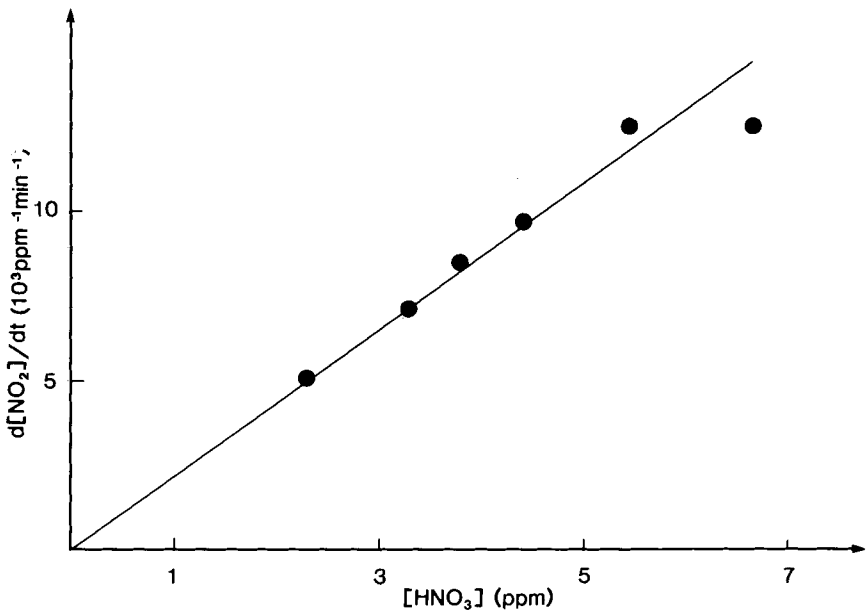

Figure 2. Formation of NO_2 from the decomposition of HNO_3 in N_2. The graph shows the measured NO_2 formation rate and the corresponding HNO_3 concentration during one experiment. The range of HNO_3 concentrations corresponds to an elapsed time of 180 min.

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TABLE II. Initial concentrations and the observed mean normalized NO_2 formation rate for some representative experiments. The mean is calculated from the 11 measurements of $d(NO_2)/dt * 1/[HNO_3]$ made during an experiment. The quoted error is one standard deviation.

Run	T (°C)	$[HNO_3]_o$ (ppm)	$[NO]_o$ (ppm)	$d[NO_2]/dt \cdot 1/[HNO_3]$ (10^3 min^{-1})
6D	22	11.9	31	3.05(±0.61)
3D	22	3.5	21	2.59(±0.94)
7D	22	10.3	16	2.50(±0.30)
2D	22	3.9	2.5	2.05(±0.28)
5D	22	8	0	2.09(±0.25)
1D	22	2.3	0	1.84(±0.61)
8D	53	7.4	18	5.00(±0.33)
9D	53	5.7	0	3.51(±0.59)
12D	3	11.5	16	1.96(±0.51)
13D	3	11.5	0	1.54(±0.51)

in opposite directions when the temperature is changed, the result would be a small apparent temperature sensitivity.

Johnston et al. [12] report a series of HNO_3 decomposition experiments undertaken at temperatures between 100 and 465°C. The reaction proceeds via two different routes. Above 400°C, a strongly temperature dependent but reactor independent reaction dominates. Below about 250°C a reaction with an activation energy of ca. 20 kJ mol^{-1} dominates. The similarity to our activation energy of 13 kJ mol^{-1} indicates that the decomposition mechanism in our case is identical to that of Johnston et al. Extrapolating Johnston's data to lower temperatures, one obtains a rate constant of about 6 10^{-3} min^{-1} for a glass reactor with a S/V ratio of 6.7 10^2 m^{-1}. Assuming a heterogeneous reaction, this value is low, compared with that of 2 10^{-3} min^{-1} obtained in

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the present work in a reactor with S/V = 14 m^{-1}. One possible explanation is a surface saturation effect at the relatively high HNO_3 concentrations used by Johnston et al.

Reaction of HNO_3 with NO

In the second set of experiments, NO was added to the reaction mixture. An increased rate of HNO_3 consumption and NO_2 production was observed, compared with the experiments with only HNO_3. The additional NO_2 production is associated with reaction (2).

(2) $$HNO_3 + NO \longrightarrow HONO + NO_2$$

However, roughly three times as much NO_2 was produced as was expected from the loss of NO and no HONO could be detected in the reaction mixture, except at high NO concentrations. The HONO produced by reaction (2) is thus rapidly consumed by reaction with HNO_3 according to (3).

(3) $$HONO + HNO_3 \longleftrightarrow 2NO_2 + H_2O$$

Kaiser and Wu [1] determined k_3 to 2.3 10^{-2} ppm^{-1} min^{-1}. Indications exists that the reaction is heterogeneous and that the rate may vary considerably in different reactors [13]. The value is large enough, compared with k_2, to give a low steady state concentration of HONO and an almost instantaneous production of two more NO_2 molecules per NO and HNO_3 initially reacted. The very low H_2O concentration, even after long times of reaction, prevented the reverse reaction (3) from influencing the results.

By assuming reactions (1)–(3) to be elementary together with a steady state approximation for HONO, the rate NO_2 production is described by Eq. (II).

(II) $$d(NO_2)/dt = k_1[HNO_3] + 3k_2[HNO_3][NO]$$

and, rearranging

(III) $$d(NO_2)/dt*1/[HNO_3]_t = k_1 + 3k_2[NO]_t$$

In the experiments selected for the rate constant evaluation, (Table II) the NO concentration did not change significantly with time. This results in $d(NO_2)/dt*1/[HNO_3]_t$ being constant with time in each experiment. The values given in Table II were calculated as the mean of the eleven observations during an experiment. A least squares fit to Eq. (III) of the 77 separate [NO] vs. $d(NO_2)/dt*1/[HNO_3]$ values gave k_2 = 1.06 (±0.05) 10^{-5} ppm^{-1} min^{-1} and k_1 = 1.99 (±0.05) 10^{-3} min^{-1}. The error limits enclose the 95% confidence interval based on the regression and does not contain systematical errors. The result from

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this treatment shows a first order dependence of reaction (2) with respect to both HNO_3 and NO.

In a study of the reaction between HNO_3 and HONO, Kaiser and Wu [1] determined k_2 at low presure to be 2.2 10^{-5} ppm^{-1} min^{-1} by following HNO_3 and HNO_2 by mass spectroscopy. Their static pyrex glass reactor has a S/V ratio of 63 m^{-1} and the authors concluded that reaction (2) was heterogeneous. McKinnon et al. [2] used a flow reactor at atmospheric pressure having an estimated S/V ratio of at least 100 m^{-1}. The experimental arrangement allowed the determination of HNO_3, NO_2, and NO by IR spectroscopy. Several different reactor surfaces were tried without significantly changing the value of k_2 of 2.1 10^{-5} ppm^{-1} min^{-1}. Since the reactor surface had little influence on the rate and since the value of k_2 agreed well with that of Kaiser and Wu [1] despite quite different methods of determination, McKinnon et al. [2] concluded that the reaction was in fact homogeneous.

Our value of k_2 of 1.1 10^{-5} ppm^{-1} min^{-1} is in fair agreement with those mentioned above. The slightly smaller value together with our smaller S/V ratio could indicate a partly heterogeneous reaction.

Streit et al. [3] reported a k_2 value of 5 10^{-7} ppm^{-1} min^{-1} which is more than an order of magnitude smaller than the other cited values. They used a pyrex reactor with an estimated S/V ratio of 21 m^{-1} and IR diode laser detection of HNO_3 and HONO. The low value of the rate constant could result from an inhibition of a possible heterogeneous reaction. Nothing in the experimental apparatus or procedure however, give any hint as to why this should be the case.

Conclusions

To estimate the possible influence on atmospheric chemistry of (2) in a polluted, urban environment, an NO concentration of 0.5 ppm and a steady HNO_3 concentration of 5 ppb is assumed. Under these conditions, 2 ppt NO and 2 ppt HNO_3 are consumed by (2) per h. Since no depletion of reactants or competing reactions have been taken into account, this is a maximum estimate and it is thus clear that (2) does not play a signficant role in the transformation of NO or HNO_3 under any set of conditions to be expected in the ambient.

The thermal decomposition of HNO_3 is a significant channel for destruction of HNO_3 in our reactor. At atmospheric pressure and 22°C about 10% per h of the HNO_3 present is decomposed through reaction (1). Since evidence exists that (1) is heterogeneous at ambient temperature, the available surface decides the decomposition rate. In the atmosphere mixing height, ground surface and aerosol loading becomes important parameters when determining the rate of HNO_3 de-

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composition. During daytime, the rate of reaction (1) in the polluted atmosphere is expected to be several orders of magnitude smaller than that obtained in the laboratory due to the low S/V ratio of the boundary layer. In a case with inversion conditions in an urban area the S/V ratio could approach 1 m^{-1} compared with 14 m^{-1} for the reactor. For this reason alone, the maximum ambient rate of reaction (1) should be at least one order of magnitude smaller than that found in our investigation.

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